

A β -Diketiminato–Nickel(II) Synthone for Nickel(I) Complexes

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Received June 29, 2005

The compound $(\text{Nacnac})\text{Ni}(\mu\text{-Br})_2\text{Li}(\text{THF})_2$ ($\text{Nacnac} = (\text{HC}(\text{CMeNC}_6\text{H}_3(i\text{-Pr})_2)_2)$) was reduced by reaction with K/Na alloy in toluene. The resulting product $[((\text{Nacnac})\text{Ni})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_5\text{-Me})]$ (**1**) was characterized and is best described as a Ni(II) species in which electron transfer from Ni to toluene has occurred. This compound reacts with a variety of donors to give Ni(I) complexes. For example, compound **1** reacts with phosphines, nitriles, acetylenes, olefins, and ketones to give the paramagnetic complexes $(\text{Nacnac})\text{Ni}(\text{PCy}_3)$ (**2**), $(\text{Nacnac})\text{Ni}(\text{Ph}_2\text{PCH}_2\text{-PPh}_2)$ (**3**), $(\text{Nacnac})\text{Ni}(\text{NCPH})$ (**4**), $(\text{Nacnac})\text{Ni}(\eta^2\text{-PhCCPh})$ (**5**), $(\text{Nacnac})\text{Ni}(\eta^2\text{-Me}_3\text{SiCCSiMe}_3)$ (**6**), $(\text{Nacnac})\text{Ni}(\eta^2\text{-H}_2\text{CCPh}_2)$ (**7**), and $(\text{Nacnac})\text{Ni}(\text{OCPh}_2)$ (**8**). In the related reaction of **1** with dimethylfulvene, electron transfer from metal to ligand is evidenced by the formation of the dimetallic species $[((\text{Nacnac})\text{Ni}(\eta^3\text{:}\eta^3\text{-C}_5\text{H}_4\text{CMe}_2))_2]$ (**9**). The crystal structures of **1–9** are reported, and the bonding and reactivity of these products are discussed.

Introduction

The study of complexes of β -diketiminato ligands (Nacnac) is an area of inorganic and organometallic chemistry that has enjoyed a resurgence in recent years. While these ligands have been used in chemistry from main-group^{1–8} to lanthanide^{3,9–12} compounds, a good deal of effort has focused on late-transition-metal derivatives,^{7,13–46} prompted in large part by the discovery of the utility of Ni–diimine complexes in olefin polymeriza-

tion.^{46–48} More recent studies have focused on the steric demands of these chelating ligands to access low-coordinate β -diketiminato complexes.^{7,13–25,47,49,50} In one such study, Puiu and Warren²⁵ described three-coordinate β -diketiminato–nickel nitrosyl complexes derived from a Ni(I) precursor. In other work employing reduced β -diketiminato complexes, Smith, Lachicotte, and Holland⁴¹ described the cleavage of N–N double bonds by a three-coordinate β -diketiminato–iron hydride complex, while Warren and co-workers³⁰ have also described the reactivity of a β -diketiminato–Co(I) toluene complex with O_2 , N_3R , and RNO . Our interest in β -diketiminato

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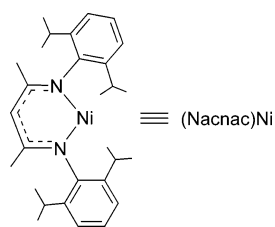
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Chart 1



complexes focuses on the synthesis and reactivity of low-valent transition-metal complexes. Mindiola and co-workers²⁹ have described reductions of β -diketiminato-Zr complexes that lead to C–N bond scission, resulting in Zr–imido derivatives, whereas reduction of β -diketiminato–Ni(II) compounds affords the three-coordinate Ni(I) complexes (Nacnac)Ni(THF) and (Nacnac)Ni(lutidine).²⁵ In this report, we describe the reduction of a β -diketiminato–Ni(II) complex in toluene (Chart 1). The resulting product has been characterized and its reactivity examined, revealing that this compound is a useful reagent for the generation of Ni(I) complexes and intermediates.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O₂-free N₂ by employing both Schlenk line techniques and a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were purified employing a Grubbs type solvent purification system manufactured by Innovative Technology. Deuterated solvents were purified using the appropriate techniques. All organic reagents were purified by conventional methods. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers. All NMR spectra were recorded in C₆D₆ at 25 °C. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe₄. EPR spectra were recorded on a X-band Bruker ESP 300E spectrometer equipped with an electromagnet capable of providing a magnetic field from 50 G to 15 kG, a gaussmeter, and a microwave counter.

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Typical measurement conditions were 20 mW microwave power, 9.7 GHz microwave frequency, 3.830 G modulation amplitude, and 4K data points covering a sweep range of 4000 G. IR spectra were recorded on a Bruker FTIR spectrometer. Combustion analyses were done in-house, employing a Perkin-Elmer CHN analyzer. In this paper, the abbreviation Nacnac refers to the β -diketiminato ligand (HC(CMe)NC₆H₃(*i*-Pr)₂)₂.

Synthesis of (Nacnac)Ni(μ -Br)₂Li(THF)₂. BuLi (2.5 M in hexane; 12 mL, 30 mmol) was added dropwise to the solution of (H₂C(CMe)NC₆H₃(*i*-Pr)₂)₂ (12.56 g, 30 mmol) in THF (50 mL) at 25 °C. Stirring was continued overnight. NiBr₂ (6.56 g, 30 mmol) was added to the above solution, and the resulting mixture was refluxed for 48 h. After concentration in vacuo, the deep green solution was kept at –35 °C for 2 days, affording dark green crystals (17.8 g) which were isolated by filtration. Yield: 17.8 g (75%). Anal. Calcd for C₃₇H₅₇Br₂LiNi₂NiO₂ (787.3): C, 56.5; H, 7.3; N, 3.6. Found: C, 56.5; H, 7.0; N, 3.4.

Synthesis of ((Nacnac)Ni)₂(μ - η^3 : η^3 -C₆H₅Me) (1). Method A. (Nacnac)Ni(μ -Br)₂Li(THF)₂ (2.222 g, 2.13 mmol) and K/Na alloy (0.066 g of K, 1.69 mmol; 0.022 g of Na, 0.96 mmol) were added to toluene (15 mL) at 25 °C and stirred for 1 week. After filtration and subsequent concentration (to 5 mL) in vacuo, the resulting deep red solution was kept at –35 °C for 1 week to isolate dark red crystals of **1** (0.53 g). After concentration of the filtrate to 3 mL, the solution was kept at –35 °C for 3 days. An additional crop of **1** was formed, affording a total yield of 0.74 g (67%).

Method B. MeMgBr (3.0 M in ether, 0.3 mL, 0.9 mmol) was added to the solution of (Nacnac)Ni(μ -Br)₂Li(THF)₂ (0.709 g, 0.90 mmol) in toluene (10 mL) at 25 °C, and the mixture was stirred overnight. After filtration and concentration in vacuo, the solution was stored at –35 °C, whereupon dark red crystals of **2** were obtained. Yield: 0.32 g (64%). IR (Nujol, cm⁻¹): 1905 (w), 1847 (w), 1789 (w), 1653 (w), 1623 (m), 1551 (s), 1517 (s), 1462 (s), 1433 (s), 1411 (s), 1318 (s), 1255 (s), 1224 (m), 1173 (s), 1098 (m), 1054 (m), 1033 (s), 930 (s), 887 (s), 842 (m), 791 (s), 759 (s), 722 (s), 631 (m), 559 (m), 543 (m), 500 (m), 436 (m). ¹H NMR (δ): 7.15–6.86 (m, 17 H, *PhMe* and *Ar*), 4.70 (s, 2 H, γ -CH), 3.91 (sept, ³J_{HH} = 7 Hz, 8 H, *CHMe*₂), 2.11 (s, 3 H, *PhMe*), 1.47 (d, ³J_{HH} = 7 Hz, 24 H, *CHMe*₂), 1.43 (s, 12 H, *CMe*), 1.11 (d, ³J_{HH} = 7 Hz, 24 H, *CHMe*₂). ¹³C{¹H} NMR (δ): 159.9 (NC), 151.6, 141.1 (*Ar*), 138.1, 129.7, 128.7, 126.0 (*PhMe*), 125.2, 123.6 (*Ar*), 98.1 (γ -C), 28.6 (*CHMe*₂), 25.2 (*PhMe*), 24.6 (*CHMe*₂), 24.4 (NCMe). EPR (toluene, 25 °C): $g = 2.20$ (broad, weak signal). EPR (toluene, –78 °C): $g = 2.14, 2.17, 2.46$. Anal. Calcd for C₆₅H₉₀N₄Ni₂ (1044.8): C, 74.7; H, 8.7; N, 5.4. Found: C, 74.3; H, 8.9; N, 5.4.

Synthesis of (Nacnac)Ni(PCy₃) (2), (Nacnac)Ni(Ph₂PCH₂PPh₂) (3), (Nacnac)Ni(NCPh) (4), (Nacnac)Ni(η^2 -PhCCPh) (5), (Nacnac)Ni(η^2 -Me₃SiCCSiMe₃) (6), (Nacnac)Ni(η^2 -H₂CCPh₂) (7), and (Nacnac)Ni(OCPh₂) (8). These compounds were prepared in a similar fashion, and thus, only one preparation is detailed. Toluene (8 mL) was added to a mixture of **1** (0.208 g, 0.20 mmol) and PCy₃ (0.112 g, 0.40 mmol) at 25 °C. The solution became pale yellow immediately. Stirring was continued for 2 h. After removal of toluene in vacuo and recrystallization in hexane at –35 °C, green-yellow crystals of **2** (0.25 g) were isolated.

Data for **2** are as follows. Yield: 0.25 g (83%). Green-yellow crystals. EPR (toluene, 25 °C): not observed. EPR (toluene, –78 °C): $g = 2.03, 2.17, 2.54$. IR (Nujol, cm⁻¹): 1904 (w), 1848 (w), 1786 (w), 1623 (w), 1550 (s), 1519 (s), 1455 (s), 1412 (s), 1316 (s), 1261 (s), 1224 (m), 1171 (s), 1098 (m), 1027 (m), 926 (m), 888 (m), 848 (m), 792 (m), 759 (m), 722 (m), 628 (m), 557 (m), 502 (m), 435 (m). Anal. Calcd for C₄₇H₇₄N₂NiP (756.8): C, 74.6; H, 9.9; N, 3.7. Found: C, 74.9; H, 10.2; N, 4.1.

Data for **3** are as follows. Yield: 0.29 g (94%). Yellow crystals. EPR (toluene, 25 °C): not observed. EPR (toluene, –78 °C): 2.03, 2.16, 2.43. IR (Nujol, cm⁻¹): 1800 (w), 1736 (w), 1620 (w), 1583 (m), 1547 (m), 1522 (s), 1461 (s), 1432 (s),

1407 (s), 1379 (s), 1357 (m), 1319 (s), 1264 (m), 1249 (m), 1225 (m), 1175 (s), 1151 (m), 1096 (s), 1055 (m), 1023 (m), 997 (m), 963 (w), 931 (m), 852 (m), 791 (m), 765 (m), 742 (s), 722 (m), 693 (s), 637 (m), 617 (w), 514 (m), 500 (m), 480 (m), 442 (m), 418 (m). Anal. Calcd for $C_{54}H_{63}N_2NiP_2$ (860.8): C, 75.4; H, 7.4; N, 3.3. Found: C, 75.0; H, 7.6; N, 3.1.

Data for **4** are as follows. Yield: 0.22 g (96%) Red crystals. EPR (toluene, 25 °C): $g = 2.19$. IR (Nujol, cm^{-1}): 2197 (s), 1913 (w), 1848 (w), 1793 (w), 1723 (w), 1621 (w), 1539 (s), 1523 (s), 1460, 1438 (s), 1408 (s), 1378 (s), 1321 (s), 1255 (m), 1229 (m), 1179 (s), 1102 (m), 1057 (m), 1026 (m), 934 (m), 795 (m), 756 (s), 720 (m), 685 (m), 653 (w), 520 (m), 443 (m). Anal. Calcd for $C_{36}H_{46}N_3Ni$ (579.5): C, 74.6; H, 8.0; N, 7.3. Found: C, 74.1; H, 8.5; N, 7.3.

Data for **5** are as follows. Yield: 0.25 g (83%). Green crystals. Crystals were $5 \cdot 0.5PhCCPh$. EPR (toluene, 25 °C): $g = 2.19$. IR (Nujol, cm^{-1}): 1852 (m), 1731 (m), 1624 (m), 1591 (w), 1531 (s), 1462 (m), 1437 (s), 1376 (s), 1317 (s), 1258 (s), 1177 (m), 1103 (m), 1066 (m), 1026 (m), 936 (m), 908 (w), 859 (m), 797 (m), 756 (s), 692 (s), 629 (m), 553 (m), 529 (m), 447 (m). Anal. Calcd for $C_{50}H_{56}N_2Ni$ (743.7): C, 80.8; H, 7.6; N, 3.8. Found: C, 80.2; H, 8.0; N, 3.8.

Data for **6** are as follows. Yield: 0.24 g (93%). Green crystals. EPR (toluene, 25 °C): $g = 2.20$. IR (Nujol, cm^{-1}): 1918 (w), 1859 (w), 1803 (s), 1626 (w), 1531 (s), 1459 (s), 1430 (s), 1393 (s), 1318 (s), 1250 (s), 1178 (s), 1107 (m), 1059 (w), 1024 (m), 932 (m), 846 (s), 795 (m), 755 (s), 701 (m), 640 (m), 520 (w), 437 (m). Anal. Calcd for $C_{37}H_{58}N_2NiSi_2$ (646.8): C, 68.7; H, 9.2; N, 4.3. Found: C, 68.3; H, 8.8; N, 4.4.

Data for **7** are as follows. Yield: 0.23 g (88%). Green crystals. EPR (toluene, 25 °C): $g = 2.22$. IR (Nujol, cm^{-1}): 1945 (w), 1911 (w), 1890 (w), 1850 (w), 1791 (w), 1728 (m), 1622 (w), 1599 (w), 1587 (w), 1577 (w), 1527 (s), 1493 (m), 1461 (s), 1434 (s), 1404 (s), 1383 (s), 1341 (m), 1314 (s), 1276 (m), 1259 (s), 1227 (m), 1178 (s), 1157 (m), 1129 (m), 1098 (s), 1056 (m), 1025 (s), 981 (w), 956 (w), 935 (s), 912 (m), 897 (m), 869 (m), 853 (m), 791 (s), 757 (s), 716 (m), 695 (s), 628 (m), 609 (m), 589 (m), 568 (m), 551 (w), 522 (m), 458 (m). Anal. Calcd for $C_{43}H_{53}N_2Ni$ (656.6): C, 78.7; H, 8.1; N, 4.3. Found: C, 78.4; H, 8.2; N, 4.3.

Data for **8** are as follows. Yield: 0.25 g (96%). Green crystals. EPR (toluene, 25 °C): $g = 2.23$. IR (Nujol, cm^{-1}): 1974 (w), 1913 (w), 1856 (w), 1817 (w), 1791 (w), 1727 (m), 1662 (m), 1646 (m), 1596 (m), 1577 (m), 1522 (s), 1463 (s), 1406 (vs), 1318 (s), 1282 (s), 1250 (s), 1227 (m), 1178 (s), 1157 (m), 1101 (s), 1075 (m), 1057 (m), 1023 (m), 934 (s), 857 (m), 844 (m), 792 (s), 761 (s), 740 (m), 695 (s), 660 (m), 634 (s), 595 (s), 531 (w), 493 (w), 439 (m). Anal. Calcd for $C_{42}H_{51}N_2NiO$ (658.6): C, 76.6; H, 7.8; N, 4.3. Found: C, 76.5; H, 7.7; N, 4.1.

Synthesis of ((Nacnac)Ni(η^3 -C₅H₄CMe₂))₂ (9**).** Dimethylfulvene (0.042 g, 0.40 mmol) was added to a solution of **1** (0.208 g, 0.20 mmol) in toluene (8 mL) at 25 °C. The mixture was stirred overnight. After concentration in vacuo, the resulting deep brown solution was kept at –35 °C for 3 days to isolate red crystals of **9**·3C₇H₈ (0.21 g, 72%). IR (Nujol, cm^{-1}):

2119 (m), 1923 (w), 1860 (w), 1797 (w), 1661 (w), 1582 (w), 1525 (s), 1467 (s), 1456 (s), 1438 (s), 1385 (s), 1377 (s), 1318 (s), 1227 (s), 1180 (s), 1102 (s), 1055 (m), 1023 (s), 936 (m), 909 (m), 857 (m), 822 (m), 793 (s), 762 (s), 716 (m), 632 (m), 552 (m), 527 (m), 506 (m), 469 (m), 454 (m). ¹H NMR (δ): 7.15–6.95 (m, 27 H, *PhMe*, *Ar*), 6.87 (tr, ³*J*_{HH} = 8 Hz, 2 H, *Ar*), 6.70 (dd, ³*J*_{HH} = 8 Hz, 2 H, *Ar*), 6.38 (t, ³*J*_{HH} = 3 Hz, 2 H, *CH*), 4.79 (s, 2 H, γ -*CH*), 4.07 (sept, ³*J*_{HH} = 7 Hz, 2 H, *CHMe*₂), 3.85 (sept, ³*J*_{HH} = 7 Hz, 2 H, *CHMe*₂), 3.45 (br t, ³*J*_{HH} = 3 Hz, 1 H, *CH*), 3.23 (sept, ³*J*_{HH} = 7 Hz, 2 H, *CHMe*₂), 3.12 (sept, ³*J*_{HH} = 7 Hz, 2 H, *CHMe*₂), 2.09 (s, 9 H, *PhMe*), 1.94 (brs, 2 H, *CH*), 1.84 (br t, ³*J*_{HH} = 3 Hz, 2 H, *CH*), 1.51 (s, 6 H, *CMe*), 1.47 (d, ³*J*_{HH} = 7 Hz, 6 H, *CHMe*₂), 1.41 (s, 6 H, *CMe*), 1.40 (dd, ³*J*_{HH} = 7 and 7 Hz, 12 H, *CHMe*₂), 1.19 (d, ³*J*_{HH} = 7 Hz, 6 H, *CHMe*₂), 1.12 (d, ³*J*_{HH} = 7 Hz, 6 H, *CHMe*₂), 1.11 (d, ³*J*_{HH} = 6 Hz, 6 H, *CHMe*₂), 1.05 (d, ³*J*_{HH} = 7 Hz, 6 H, *CHMe*₂), 0.96 (d,

³*J*_{HH} = 7 Hz, 6 H, *CHMe*₂), 0.94 (s, 6 H, C=*CMeMe*), 0.50 (s, 6 H, C=*CMeMe*). ¹³C{¹H} NMR (δ): 160.4, 151.9 (NC), 125.5, 151.9, 142.9, 141.4, 141.1, 140.2, 140.8, 124.7, 123.9, 123.8, 123.8 (*Ar*), 123.7 (C=*CMe*₂), 120.4 (C=*CMe*₂), 99.3 (γ -C), 97.1, 77.0, 66.2, 47.7 (CH), 29.4, 28.4, 28.3, 27.7 (*CHMe*₂), 25.7, 25.1, 24.9, 24.6, 24.4, 24.0, 24.0, 23.9 (*CHMe*₂), 23.9, 22.7 (*NCMe*). Anal. Calcd for $C_{74}H_{102}N_4Ni_2$ (1165.1): C, 76.3; H, 8.8; N, 4.8. Found: C, 76.1; H, 9.0; N, 4.8.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O₂-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1448 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5^\circ < 2\theta < 45-50.0^\circ$). The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.⁵¹ The heavy-atom positions were determined using direct methods employing the SHELXTL direct-methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F , minimizing the function $w(F_o - F_c)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. In the case of compound **1** the methyl group of toluene was modeled by a 50:50 two-site disorder. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C–H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Crystallographic data and structure solution and refinement details are given in Table 1.

Results and Discussion

The compound (Nacnac)Ni(μ -Br)₂Li(THF)₂ was reduced by reaction with K/Na alloy at 25 °C for 1 week in toluene. After filtration, concentration, and storage of the solution at –35 °C dark red crystals of **1** were formed. Isolation of a second crop of product in a similar manner afforded a total yield of 67%. In a similar fashion treatment of (Nacnac)Ni(μ -Br)₂Li(THF)₂ with MeMgBr in toluene resulted in reduction and the formation of **1** in 64% yield. The ¹H NMR spectrum of **1** is composed of sharp resonances indicative of a diamagnetic compound (Figure 1). The elemental analyses were consistent with a β -diketiminato ligand-to-toluene ratio of 2:1, while a single-crystal X-ray crys-

(51) Cromer, D. T.; Waber, J. T. *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, pp 71–147.

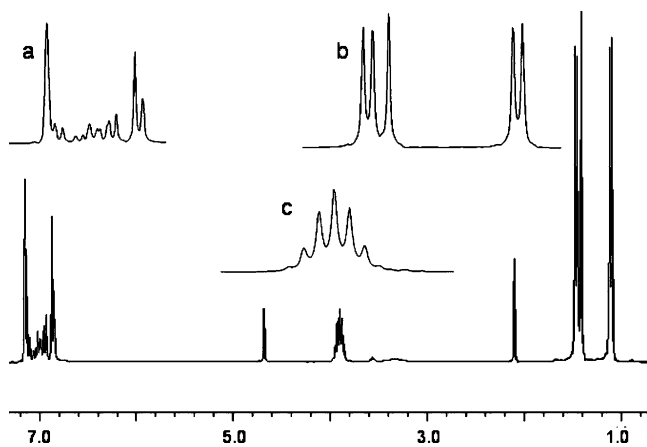


Figure 1. ^1H NMR spectrum of **1**. Expansions of the aromatic, methine, and methyl resonances are shown in a–c, respectively.

tallographic study revealed the formulation of **1** as $(\text{Nacnac})\text{Ni}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_5\text{Me})$ (Figure 2). The Ni is coordinated to two N atoms at distances of 1.894(6) and 1.930(4) Å and interacts with the sides of the 2-fold disordered toluene molecule in an $\eta^3\text{:}\eta^3$ manner. The crystallographic symmetry constrains the two NiN_2 planes to be parallel to each other and results in an angle of 88° between NiN_2 planes and the plane of the toluene molecule. The Ni–C distances of 2.185(6), 1.980(5), and 2.209(5) Å are reminiscent of a Ni–allyl fragment. The C–C (C30–C32') distances between the allyl fragments are 1.445(9) Å. This geometry, together with the diamagnetic nature of **1**, supports the notion that electron transfer from Ni to toluene has occurred, affording a compound containing two Ni(II) centers and a bridging dianionic toluene fragment. Single-electron transfer to toluene has been previously described by Lappert and co-workers in the presentation of the compound $(18\text{-crown-6})\text{K}(\eta^6\text{-C}_6\text{H}_5\text{Me})$.⁵²

Highly concentrated toluene solutions of compound **1** (18 mg in 0.2 mL) reveal a broad, weak, but discernible EPR signal with $g = 2.20$ at room temperature. At low temperature, frozen solutions of **1** exhibit a weak axial

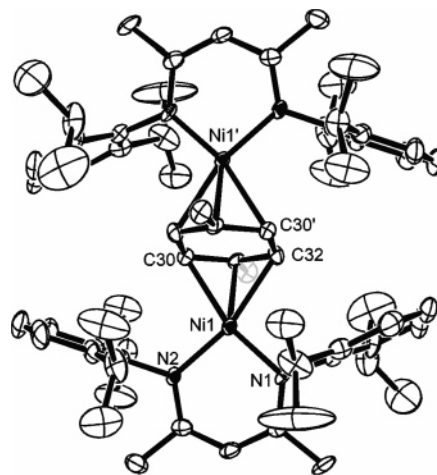


Figure 2. ORTEP drawing of **1**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. One position of the disordered toluene methyl group is shown in gray. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.894(6), Ni(1)–N(2) = 1.930(4), Ni(1)–C(31) = 1.980(5), Ni(1)–C(30) = 2.185(6), Ni(1)–C(32) = 2.209(5), C(30)–C(31) = 1.425(9), C(30)–C(32') = 1.445(9), C(31)–C(32) = 1.412(8); N(1)–Ni(1)–N(2) = $96.48(19)$.

signal. The g values of 2.14, 2.17, and 2.46 were determined via simulation. This compares with the signals at 2.068, 2.133, and 2.435 reported for $(\text{HC}(\text{CMeNc}_6\text{H}_3\text{Me}_2)_2)\text{Ni}(2,4\text{-lutidine})$.⁵⁰ While the solid-state structure and NMR data support a Ni(II) formulation, the observation of a weak EPR signal for **1** suggest that a Ni(I) species is accessible in solution. This view is further supported by the reactivity of **1**. For example, compound **1** reacts with the phosphines PCy_3 and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ to give the paramagnetic complexes $(\text{Nacnac})\text{Ni}(\text{PCy}_3)$ (**2**) and $(\text{Nacnac})\text{Ni}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ (**3**), respectively (Scheme 1). These products do not give rise to an EPR signal at 25°C in solution; however, in frozen toluene solution at -78°C these species gave similar spectra (Figure 3). Spectral simulations were used to determine the g values. This coupling is consistent with a single Ni–P bond in both complexes.

Table 1. Crystallographic Data

| | 1 | 2 | 3 | 4 | 5:0.5PhCCPh | 6 | 7 | 8 | 9:3(toluene) |
|--|---|--|--|---|---|---|---|--|--|
| formula | $\text{C}_{65}\text{H}_{90}\text{N}_4\text{Ni}_2$ | $\text{C}_{47}\text{H}_{74}\text{N}_2\text{NiP}$ | $\text{C}_{54}\text{H}_{64}\text{N}_2\text{NiP}_2$ | $\text{C}_{36}\text{H}_{46}\text{N}_3\text{Ni}$ | $\text{C}_{50}\text{H}_{56}\text{N}_2\text{Ni}$ | $\text{C}_{37}\text{H}_{59}\text{N}_2\text{NiSi}_2$ | $\text{C}_{43}\text{H}_{53}\text{N}_2\text{Ni}$ | $\text{C}_{42}\text{H}_{51}\text{N}_2\text{NiO}$ | $\text{C}_{95}\text{H}_{126}\text{N}_4\text{Ni}_2$ |
| formula wt | 1044.82 | 756.76 | 861.72 | 579.47 | 743.68 | 646.75 | 656.58 | 658.56 | 1441.42 |
| cryst syst | monoclinic | monoclinic | orthorhombic | monoclinic | triclinic | orthorhombic | monoclinic | monoclinic | triclinic |
| space group | $P2_1/n$ | $P2_1$ | $P2_12_12_1$ | $P2_1/n$ | $P\bar{1}$ | $Pbcn$ | $P2_1/n$ | $C2/c$ | $P\bar{1}$ |
| a (Å) | 10.783(3) | 11.2919(6) | 13.4602(8) | 8.722(3) | 9.9381(19) | 10.7774(16) | 11.995(5) | 53.177(10) | 13.3750(16) |
| b (Å) | 19.725(6) | 17.6025(9) | 18.2396(12) | 15.043(5) | 10.815(2) | 17.672(3) | 22.680(11) | 9.1830(17) | 14.8811(18) |
| c (Å) | 14.118(4) | 11.7930(6) | 19.8633(12) | 25.743(8) | 20.289(4) | 21.089(3) | 13.875(7) | 40.478(8) | 24.154(3) |
| α (deg) | | | | | 86.755(4) | | | | 104.371(2) |
| β (deg) | 94.810(10) | 108.8510(10) | | 95.613(7) | 82.996(4) | | 97.749(11) | 130.063(2) | 93.535(2) |
| γ (deg) | | | | | 80.134(3) | | | | 109.941(2) |
| V (Å ³) | 2992.2(14) | 2218.3(2) | 4876.6(5) | 3361.5(19) | 2130.9(7) | 4016.5(10) | 3740(3) | 15128(5) | 4320.9(9) |
| Z | 2 | 2 | 4 | 4 | 2 | 4 | 4 | 16 | 2 |
| d (calcd) (g cm ⁻³) | 1.160 | 1.133 | 1.174 | 1.145 | 1.159 | 1.070 | 1.166 | 1.157 | 1.108 |
| abs coeff, μ (mm ⁻¹) | 0.670 | 0.505 | 0.500 | 0.603 | 0.490 | 0.567 | 0.549 | 0.545 | 0.481 |
| no. of data collected | 4276 | 11 041 | 24 116 | 15 561 | 4950 | 36 415 | 13 603 | 70 936 | 36 457 |
| R (int) | 0.0162 | 0.0197 | 0.0490 | 0.1190 | 0.0259 | 0.0461 | 0.0804 | 0.1954 | 0.0676 |
| no. of data, $F_o^2 > 3\sigma(F_o^2)$ | 2775 | 6297 | 7030 | 4896 | 3356 | 3534 | 5476 | 13 294 | 12 530 |
| no. of variables | 325 | 460 | 532 | 361 | 478 | 191 | 415 | 829 | 754 |
| R | 0.0727 | 0.0325 | 0.0392 | 0.0808 | 0.0737 | 0.0522 | 0.0605 | 0.0821 | 0.0837 |
| R_w | 0.1769 | 0.0779 | 0.0885 | 0.1892 | 0.2118 | 0.1383 | 0.1302 | 0.1847 | 0.2235 |
| GOF | 1.016 | 1.024 | 0.988 | 1.009 | 1.126 | 1.031 | 1.009 | 0.988 | 1.006 |

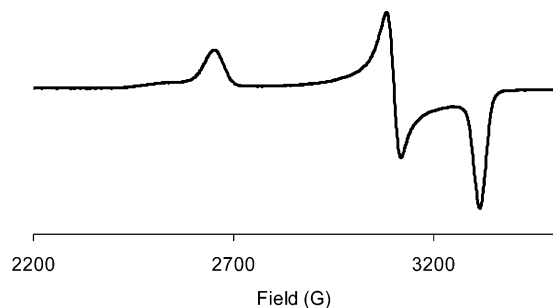


Figure 3. Frozen toluene solution EPR spectrum of **2**. g values of 2.14, 2.17, and 2.45 were determined by spectral simulation.

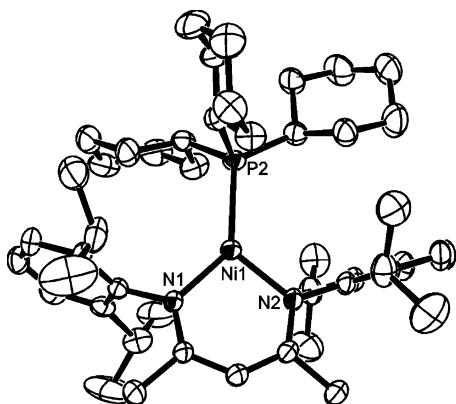
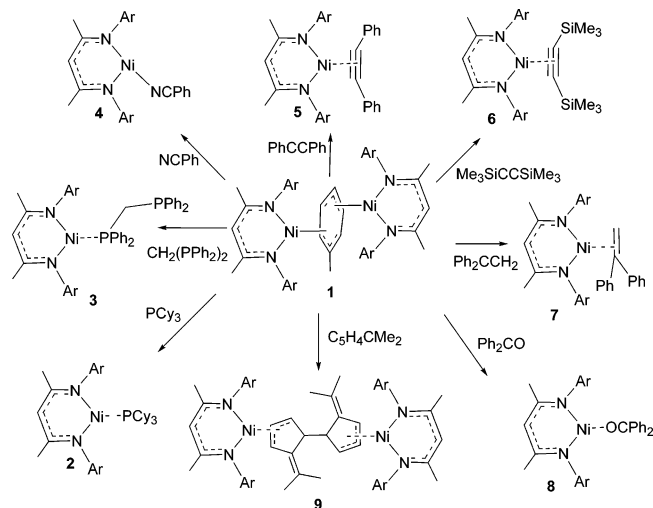


Figure 4. ORTEP drawing of **2**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.943(2), Ni(1)–N(2) = 1.957(2), Ni(1)–P(1) = 2.2786(8); N(1)–Ni(1)–N(2) = 96.70(9), N(1)–Ni(1)–P(1) = 135.43(6), N(2)–Ni(1)–P(1) = 127.25(7).

Scheme 1



These formulas were confirmed via crystallographic studies (Figures 4 and 5). In these compounds, the Ni atom is three-coordinate. In **2**, the Ni–N distances are 1.943(2) and 1.957(2) Å and the Ni–P distance is 2.2786(8) Å, whereas in **3**, the corresponding distances are 1.889(3), 1.935(3), and 2.2150(9) Å. The Ni(I) centers reside in pseudo-trigonal-planar coordination spheres with chelate bite angles of 96.70(9) and 96.44(12)° in **2**

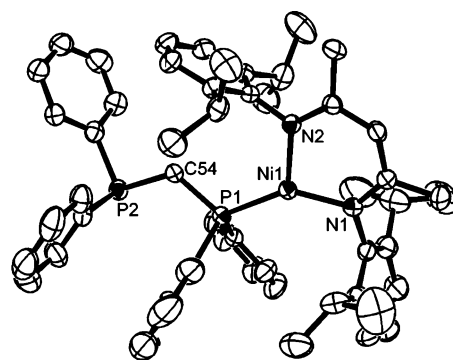


Figure 5. ORTEP drawing of **3**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.889(3), Ni(1)–N(2) = 1.935(3), Ni(1)–P(1) = 2.2150(9); N(1)–Ni(1)–N(2) = 96.44(12), N(1)–Ni(1)–P(1) = 142.96(9), N(2)–Ni(1)–P(1) = 120.56(9).

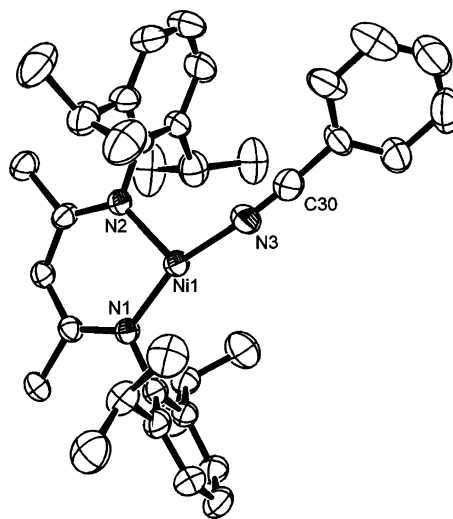


Figure 6. ORTEP drawing of **4**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(3) = 1.811(6), Ni(1)–N(1) = 1.848(5), Ni(1)–N(2) = 1.920(4), N(3)–C(30) = 1.183(8); N(3)–Ni(1)–N(1) = 158.8(2), N(3)–Ni(1)–N(2) = 103.1(2), N(1)–Ni(1)–N(2) = 97.88(18), C(30)–N(3)–Ni(1) = 172.8(6), N(3)–C(30)–C(31) = 176.2(7).

and **3**, respectively. The N–Ni–P angles are 135.43(6) and 127.25(7)° in **2** and 142.96(9) and 120.56(9)° in **3**. The longer Ni–P bond in **2** results from that the greater steric demands of PCy₃, despite its greater basicity in comparison to Ph₂PCH₂PPh₂. Similarly, the distortion of the geometry about Ni in **3** is consistent with a sterically crowded coordination site and the dissymmetric nature of the monodentate coordinating phosphine Ph₂PCH₂PPh₂.

In a similar fashion, compound **1** reacts with PhCN to give a Ni(I) coordination complex, formulated as (Nacnac)Ni(NCPh) (**4**) (Scheme 1) on the basis of EPR spectroscopy and confirmed by crystallography (Figure 6). The Ni–N bond lengths in **4** for the Nacnac ligand were found to be 1.848(5) and 1.920(4) Å, while the N–Ni–N chelate bite angle is 97.88(18)°. This geometry is similar to those described above. The Ni–N bond distance for the coordinated nitrile was found to be 1.811(6) Å, consistent with strong σ donation. However, the geometry about Ni is not symmetric. The Nacnac ligand N atoms form angles with the coordinated

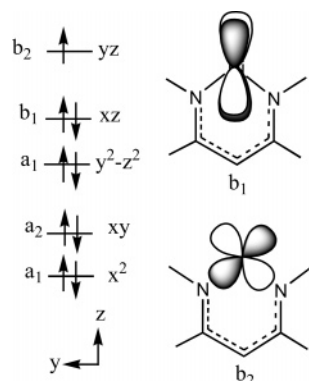


Figure 7. Frontier orbitals of (Nacnac)NiL.

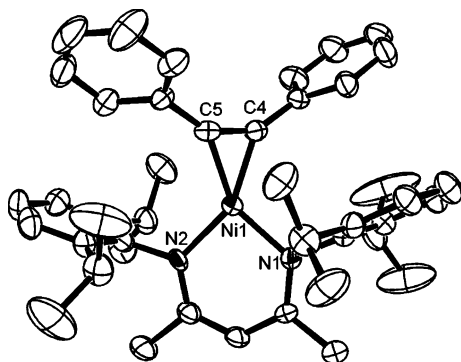


Figure 8. ORTEP drawing of **5**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–C(4) = 1.906(9), Ni(1)–C(5) = 1.914(8), Ni(1)–N(2) = 1.917(7), Ni(1)–N(1) = 1.920(7); C(5)–Ni(1)–N(2) = 118.2(4), C(4)–Ni(1)–N(1) = 114.8(4), C(5)–Ni(1)–N(1) = 143.7(4), N(2)–Ni(1)–N(1) = 94.7(3), C(5)–C(4)–Ni(1) = 71.0(6), C(4)–C(5)–Ni(1) = 70.3(5).

benzotrile N of 158.8(2) and 103.1(2)°. This geometry about Ni is best described as a pseudo-T-shaped. Nonetheless, the geometry of the nitrile is linear as expected, with C–N–Ni and N–C–C angles of 172.8(6) and 176.2(7)°, respectively. Similar geometries have been described for (Nacnac)Ni(2,4-lutidine).⁵⁰

The differing geometries of **2–4** can be understood by consideration of the (Nacnac)NiX frontier orbitals described by Holland and co-workers.^{17,19} Addition of an electron to the Ni(II) frontier orbitals fills the b_1 orbital in the xz plane, leaving the HOMO as the singly occupied b_2 orbital in the yz plane. In the case of **4**, donation from the N of the nitrile to this SOMO is consistent with the “T-shaped” coordination sphere about Ni. The closer approach of the geometry of the phosphine adducts **2** and **3** to trigonal-planar geometry may result from the steric issues discussed above. However, this geometry also provides for the π back-donation from Ni to phosphorus (Figure 7).

Compound **1** also reacts with the acetylenes PhCCPh and Me₃SiCCSiMe₃, resulting in the formation of the crystalline products (Nacnac)Ni(η^2 -PhCCPh) (**5**) and (Nacnac)Ni(η^2 -Me₃SiCCSiMe₃) (**6**) in yields of 83% and 93%, respectively (Scheme 1). Crystallographic studies of **5**·0.5PhCCPh and **6** (Figures 8 and 9) confirmed these formulations. In these compounds, the Ni centers are four-coordinate with coordination of the Nacnac ligand and the acetylene. In the case of **6**, crystallographic site symmetry imposes a C_2 axis on the molecule. Nonethe-

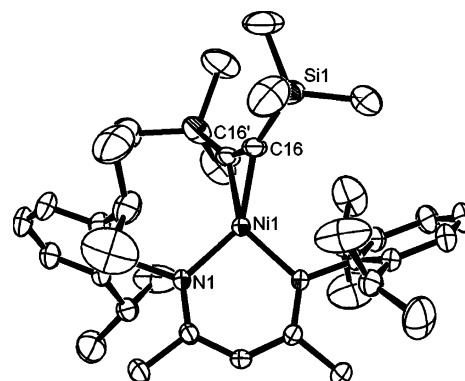


Figure 9. ORTEP drawing of **6**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.944(2), Ni(1)–C(16) = 1.960(3), C(16)–C(16') = 1.250(7); N(1)–Ni(1)–N(1) = 94.97(15), N(1)–Ni(1)–C(16) = 121.32(13), N(1)–Ni(1)–C(16) = 139.56(14), N(1)–Ni(1)–C(16) = 139.56(14), N(1)–Ni(1)–C(16) = 121.32(13), C(16)–C(16)–Si(1) = 147.09(11), C(16)–C(16)–Ni(1) = 71.40(10), Si(1)–C(16)–Ni(1) = 141.5(2).

less, the geometries about Ni in both products are neither square planar nor tetrahedral. The angles between the NiN₂ and NiC₂ planes were found to be 37.9 and 59.1° for **5** and **6**, respectively. These distorted geometries reflect the steric congestion resulting from interaction of the sterically demanding Nacnac ligand and acetylene substituents. The Ni–N distances are 1.917(7) and 1.920(7) Å in **5** and 1.944(2) Å in **6**, while the ligand bite angles are 94.7(3) and 94.97(15)° in **5** and **6**, respectively. These Ni–N bond lengths are similar to those seen above for the Ni(I) products and significantly longer than those seen in the Ni(III)–imido compound (Nacnac)Ni=NAd (1.884(2), 1.874(2) Å).⁵⁰ The Ni–C distances were found to be 1.906(9) and 1.914(8) Å in **5** and 1.960(3) Å in **6**. The longer Ni–C distance in **6** reflects the greater steric demands of the acetylene substituents. Nonetheless, the geometries about the acetylenic carbons in **5** and **6** are similar, as revealed by Ni–C–C_{Ph} angles of 141.1(7) and 146.7(8)° and C–C–C_{Ph} angles of 147.0(9) and 141.9(6)° in **5** and the corresponding Ni–C–Si and C–C–Si angles of 141.5(2) and 147.09(11)° respectively in **6**. These “bend-back” angles suggest the possibility of electron donation from the Ni to the acetylenic π^* orbitals. However, this is not reflected in the acetylenic C–C bond distances of 1.266(14) and 1.250(7) Å in **5** and **6**, respectively. These metric data are consistent with the view that the products are best viewed as Ni(I)–acetylene adducts rather than Ni(III) metallacycles.

A closely related situation results in the product of the reaction of **1** with the olefin Ph₂CCH₂. This reaction gives the product (Nacnac)Ni(η^2 -H₂CCPh₂) (**7**) in 88% isolated yield (Scheme 1). This species gives rise to a broad EPR resonance in solution at $g = 2.22$. A crystallographic study (Figure 10) of **7** revealed that, similar to **5** and **6**, compound **7** is four-coordinate. However, the geometry about Ni is best described as pseudo square planar, as the angle between the NiN₂ and the NiC₂ plane is only 13.1°. Despite the difference in geometry at Ni, the Nacnac–Ni parameters in **7** are similar to those in **5** and **6** (Ni–N = 1.902(4), 1.943(4) Å, N–Ni–N = 97.03(17)°). The Ni–C bond lengths were found to be

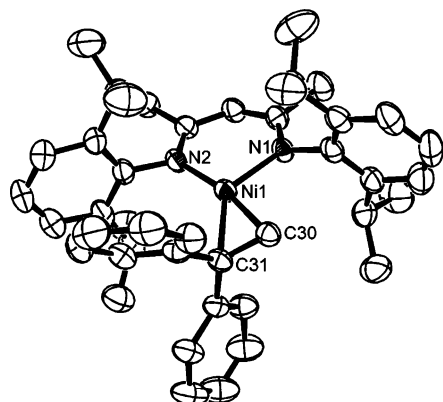


Figure 10. ORTEP drawing of **7**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(2) = 1.902(4), Ni(1)–N(1) = 1.943(4), Ni(1)–C(30) = 1.982(5), Ni(1)–C(31) = 2.088(5), C(30)–C(31) = 1.391(6); N(2)–Ni(1)–N(1) = 97.03(17), N(2)–Ni(1)–C(30) = 168.20(18), N(1)–Ni(1)–C(30) = 94.72(19), N(2)–Ni(1)–C(31) = 128.45(19), N(1)–Ni(1)–C(31) = 133.16(19), C(31)–C(30)–Ni(1) = 74.2(3), C(30)–C(31)–Ni(1) = 66.0(3).

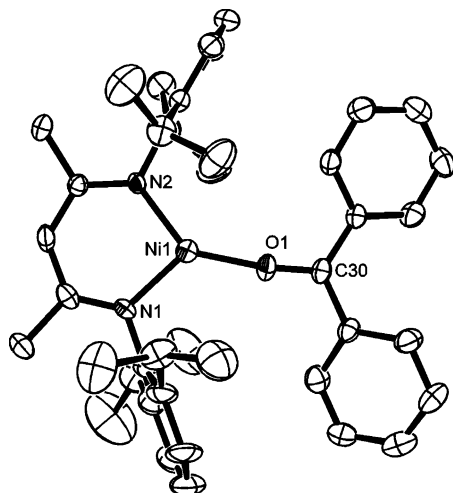


Figure 11. ORTEP drawing of one of the two molecules of **8** in the asymmetric unit, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–O(1) = 1.825(5), Ni(1)–N(2) = 1.899(5), Ni(1)–N(1) = 1.910(5), O(1)–C(30) = 1.239(7); O(1)–Ni(1)–N(2) = 138.2(2), O(1)–Ni(1)–N(1) = 125.0(2), N(2)–Ni(1)–N(1) = 96.7(2), C(30)–O(1)–Ni(1) = 172.0(5).

1.982(5) and 2.088(5) Å, with the latter longer bond resulting from the substituted carbon of the olefin. These distances are significantly longer than the Ni–C distances seen in the acetylene adducts **5** and **6**, consistent with the poorer donor ability of olefins as well as the additional steric demands provided by the phenyl substituents of Ph₂CCH₂. The olefinic C–C bond length of 1.391(6) Å and the sum of the C–C–C angles about the substituted olefinic carbon of 357.5° indicate little perturbation of the olefin upon coordination to Ni.

In the related reaction of **1** with Ph₂CO, the paramagnetic Ni(I) complex (Nacnac)Ni(OCPh₂) (**8**) is formed in 96% isolated yield (Scheme 1). While only weakly diffracting crystals could be obtained, X-ray crystallographic data (Figure 11) for this product did confirm pseudo-trigonal-planar geometry about Ni with Ni–N bond lengths of 1.899(5) and 1.910(5) Å and a Ni–O

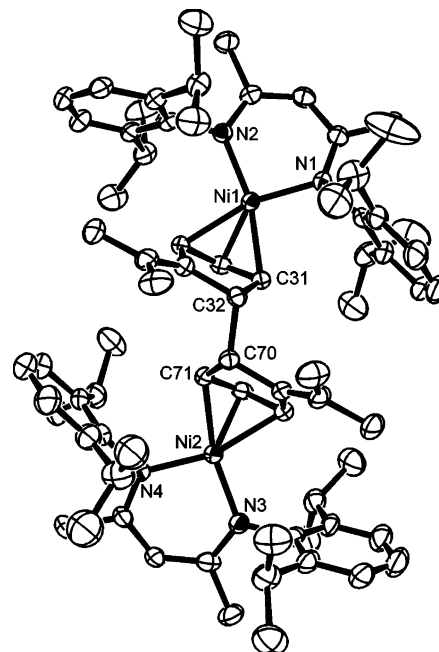


Figure 12. ORTEP drawing of **9**, with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.917(5), Ni(1)–N(2) = 1.930(5), Ni(1)–C(30) = 1.915(6), Ni(1)–C(31) = 2.029(6), Ni(1)–C(34) = 2.112(6), Ni(2)–N(3) = 1.917(5), Ni(2)–N(4) = 1.918(5), Ni(2)–C(67) = 1.925(6), Ni(2)–C(68) = 2.112(6), Ni(2)–C(71) = 2.005(6), C(30)–C(31) = 1.404(8), C(30)–C(34) = 1.407(9), C(31)–C(32) = 1.523(8), C(32)–C(33) = 1.519(8), C(32)–C(70) = 1.573(8), C(33)–C(35) = 1.371(9), C(33)–C(34) = 1.453(9), C(67)–C(71) = 1.377(9), C(67)–C(68) = 1.425(9), C(68)–C(69) = 1.455(9), C(69)–C(72) = 1.340(9), C(69)–C(70) = 1.527(8), C(70)–C(71) = 1.517(9), C(72)–C(73) = 1.506(10), C(72)–C(74) = 1.521(12); C(30)–Ni(1)–N(1) = 127.0(3), C(30)–Ni(1)–N(2) = 125.2(3), N(1)–Ni(1)–N(2) = 96.0(2), N(3)–Ni(2)–N(4) = 96.5(2).

distance of 1.825(5) Å. The bite angle for the Nacnac ligand is similar to those above at 96.7(2)°, while the N–Ni–O angles were found to be 138.2(2) and 125.0(2)°. The geometry at O is approximately linear, with a Ni–O–C angle of 172.0(5)°. The C–O bond distance is 1.239(7) Å. This orientation may reflect the steric crowding within the coordination site as a result of interactions of the ketonic aryl groups with the aryl substituents on the Nacnac ligand. In addition, the geometry at O allows for electron donation to the HOMO (b₂) on Ni and for π back-donation from the filled Ni b₁ orbital to the π^* orbital of the carbonyl fragment. The degree of electron transfer from Ni to ligand is an interesting aspect of this compound. If electron transfer from the metal to the ligand occurred, then **8** could be formulated as a Ni(II)–benzophenone radical anion. However, the EPR signal for **8** gives rise to a resonance at $g = 2.23$. This is typical of the formally Ni(I) species and distinct from carbon-based radicals, thus implying that the unpaired electron resides in a metal-based orbital and supporting a Ni(I)–benzophenone adduct description.

The possibility of metal-to-ligand electron transfer was demonstrated in the reaction of **1** with dimethylfulvene. Stirring of the reaction mixture in toluene at 25 °C overnight resulted in a deep brown solution. Following concentration of the solution and storage at

–35 °C of the solution red crystals of **9**·3C₇H₈ were isolated in 72% yield. The ¹H and ¹³C{¹H} NMR spectra of **9** confirmed the presence of the ligand and fulvene fragments. The methyl groups of the dimethylfulvene fragments were inequivalent, exhibiting ¹H NMR resonances at 0.50 and 0.94 ppm. These data together with the observation of the ¹³C{¹H} NMR resonance at 47.7 ppm corresponding to a methine carbon suggest dimerization of via coupling of two dimethylfulvene units. A crystallographic study confirmed that crystals of **9**·3C₇H₈ formed in toluene were formulated as [(Nacnac)-Ni]₂(η³:η³-C₅H₄CMe₂)₂·3C₇H₈ (Scheme 1). In this compound, two (Nacnac)Ni centers bind to linked fulvenide fragments in η³ fashions (Figure 12). The two fulvenide fragments are linked by a typical C–C single bond (1.573(8) Å) between the carbons α to the dimethylmethylene substituents. This geometry about the Ni centers in **9** is reminiscent of that seen in **1**. The Ni–N bond distances are 1.917(5), 1.930(5), 1.917(5), and 1.918(5) Å, and the chelate rings form N–Ni–N angles of 96.0(2) and 96.5(2)°. The fulvenide fragments coordinate to the metal in an η³ fashion with Ni(1)–C distances of 1.915(6), 2.029(6), and 2.112(6) Å and Ni(2)–C distances of 1.925(6), 2.112(6), and 2.005(6) Å, affording a geometry reminiscent of Ni(II)–allyl complexes. The formation of the diamagnetic product **9** is

thought to proceed via exchange of dimethylfulvene for toluene at Ni, followed by electron transfer from Ni to the fulvene fragment and C–C coupling of the carbon-based radicals.

Summary

Compound **1** is diamagnetic and is thus formulated as a Ni(II) product. Nonetheless, it reacts in a facile manner with a variety of donors such as phosphines, nitriles, acetylenes, olefins, and ketones to give Ni(I) compounds. The M–L interaction involves both ligand-to-metal σ donation and metal-to-ligand π donation. Electron transfer from the metal to the ligand was demonstrated in the case of the reaction of **1** with dimethylfulvene, where C–C coupling gives the difulvenide bimetallic complex **9**.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050544F